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Anomalous magnetic antiresonance and resonance in ferrite nanoparticles embedded in opal matrix

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ABSTRACT

Observation of magnetic antiresonance phenomenon is reported in 3D opal nanocomposite with embedded ferrite particles. Antiresonance at microwave frequencies of millimeter waveband was observed. It results in a sharp maximum of the reflection coefficient of an electromagnetic wave. Measurements were carried out in the frequency range from 26 to 38 GHz for two compositions of embedded ferrite particles, namely, the $Co_{0.5}Zn_{0.5}Fe_2O_4$ and $Ni_{0.5}Zn_{0.5}Fe_2O_4$. The physical nature of antiresonance is discussed.

1. Introduction

Investigation and application of extraordinary electromagnetic properties of metamaterials and nanocomposites become one of the most promising topics in previous years [1,2]. Numerous efforts are undertaken for utilization of this class of materials in optical and microwave devices. Magneto-optical properties of the magnetic photonic crystals as well as of the photonic crystals with magnetic defects have been considered [3], and it has been theoretically shown that the effect of strong photon confinement near the defect leads to enhancement of nonlinear and nonreciprocal optical properties. New phenomena were discovered at microwave frequencies in the case when a wave passes a nanocomposite. The focusing of a microwave beam was demonstrated experimentally for a plate of a negative-index material. The possibilities of applications of such magnetic materials as sensing elements in high resolution scanning magnetic resonance microscopy [4] and magnetic nanoparticles for detection of biomolecules [5] have been demonstrated.

Three-dimensional magnetic photonic crystals based on artificial opals impregnated by Bi-substituted yttrium-iron garnet were fabricated [6]. Generation of second harmonic in the vicinity of photonic band gap and the transversal Kerr effect in magnetic field was investigated. The effects of transmission and reflection of light through 3D magnetic photonic crystals with embedded magnetite particles, based on an artificial opal matrix, were investigated. Strong enhancement of the polar Kerr effect near the photonic band gap was found [7].

Considerable progress was achieved in the studies and explanation of microwave properties of the 3D-nanocomposites. Propagation of the guided waves in a negative-index media was thoroughly investigated. In particular, the guided waves in planar and coupled-cavity waveguides incorporating a 3D layered photonic crystal were studied [8]. It was shown that full transmission through the waveguide structure is possible.

The problem of interaction between electromagnetic wave and magnetic nanoparticles is of essential interest. Today investigations are aimed at synthesis of new magnetic materials with improved properties. Methods of preparation of the Ni-coated strontium ferrite powder with excellent microwave absorption properties in the centimeter waveband were reported in [9]. New 3D magnetic photonic crystals have been synthesized in a matrix of latex spheres 200 nm in diameter containing magnetite particles [10]. Nanocrystalline zinc doped nickel ferrite thin films with low dielectric constant were fabricated by spin-deposition technique [11,12]. Their magnetic properties and microwave complex permittivity were investigated. Magnetic resonance in nanoparticles is of special interest for possible applications. The dynamical response of nanoparticles was investigated theoretically within the model based on Landau–Lifshitz–Gilbert equations. The shape of resonance line was calculated for different temperatures. From these data the parameters of the resonance field shift and the linewidth were extracted [13].

From the above incomplete list of references one could conclude that significant efforts are now undertaken for the development of new composites and metamaterials, which permit to realize new functional possibilities of microwave electronic

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devices. The opal matrix class of artificial materials is especially suitable for constructing magnetically tunable microwave materials. One may regard the opal matrix package with embedded magnetic nanoparticles as a promising material for application in attenuators, phase shifters, filters and other devices of centimeter and millimeter wavebands. From the results of [11,12] it can be concluded that the nickel–zinc, cobalt–zinc and other ferrites with the spinel structure can be considered as materials, which can be inserted in the inter-sphere voids of an opal matrix. This conclusion is based on the attracting combination of physical properties of spinel ferrites, such as relatively high saturation magnetization, low anisotropy at room temperature, high Curie temperature, high resistance, low dielectric losses and chemical stability.

Resonance phenomena in 3D opal-based nanocomposites are studied in this work by the investigations of the frequency and magnetic field dependences of the transmission and reflection coefficients at the millimeter waveband. Experiments are carried out with the samples of the nanocomposites containing the particles of nickel–zinc and cobalt–zinc ferrites. Under the conditions of magnetic resonance variations of microwave signal transmitted through a sample or reflected from it are mostly due to changes in the surface impedance and absorption of electromagnetic wave. It is shown that the amplitude of a transmitted wave sharply decreases in resonance. The giant increase of the reflected wave amplitude was discovered in magnetic fields less than the resonance field.

2. Experimental

Few methods for synthesis of opal matrices, inverse opal matrices and films have been developed till date [14,15]. In these works, special attention has been paid to methods of characterization of their structure. Our goal was to obtain the nanocomposite with the ferrite nanoparticles embedded in the inter-sphere voids. Insertion of the particles was made by means of repeated impregnation. We needed the technology, which permits to fabricate the opal matrix packages with improved mechanical properties, namely with better adhesion between spheres. The opal matrix packages with sphere diameter of 250 nm were obtained by the following method. First, the nanoparticles of amorphous SiO_2 were synthesized by hydrolysis reaction between tetra-ether of ortho-silicon acid $Si(OC_2H_5)_4$ and ethanol C_2H_5OH in the presence of ammonium hydroxide NH_4OH as a catalyst. As the result of this reaction small ramified nanoparticles were obtained and then they were transformed to the spherical monodisperse silicon dioxide particles by the polycondensation process. After impregnation and drying the material was thermally treated in order to strengthen it and remove residual water. Characterization of structural perfection of the packages obtained was carried out optically by examination of the shape and width of Bragg reflection bands.

Infusion is one of the simplest methods to insert any chemical element or compounds into the opal matrices. This method uses the so-called precursor, which is a substance of definite chemical composition, which after corresponding thermal treatment transforms into the desired substance in the inter-sphere voids. In order to obtain the ferrite nanoparticles, the precursors must be well soluble in water and converted into oxides at moderate temperatures. In this work the soluble nitrates were used as the precursors. Thermal treatment was carried out at temperatures from 770 to 870 K. Infusion and afterheating have been repeated up to 20 times. This procedure resulted in gradual filling of the inter-sphere voids. The volume concentration of the inserted phases was typically about 3–5%. X-ray analysis confirmed that most of the inserted material corresponds to the spinel-type phases like $ZnFe_2O_4$ and $(Ni_XZn_{1-X})Fe_2O_4$, although some other iron-containing phases were present. For the sake of simplicity and despite the presence of additional phases, we shall call nanoparticles as nickel–zinc and cobalt–zinc ferrites. The inserted particles have polycrystalline structure and irregular shape. The typical size of the particles was in the interval from 5 to 60 nm. The dark-field TEM image of the 3D-nanocomposite structure with Ni–Zn ferrite-spinel particles is shown in Fig. 1a. The important feature seen in Fig. 1a, is that the particles form clusters, in which the individual particles are located very close to one another at distances of few nanometers and even less. These aggregates of the particles were obtained, mostly, due the fact that infusion and thermal treatment have been repeated many times and several particles could be obtained inside one void.

Using this procedure the samples of opal matrices with embedded nickel–zinc and cobalt–zinc ferrite particles were obtained. Apart from the perfect close-packed structure, the peculiarity of our samples was in their higher strength.

Measurement of magnetization curves is a useful method for the characterization of magnetic photonic crystals. For nanocomposite with Ni–Zn ferrite particles the magnetization curve is shown in Fig. 1b. In low fields, the magnetization raises sharply. This behavior can be considered as an evidence for the presence of a magnetically ordered ferrite phase. However, full saturation was

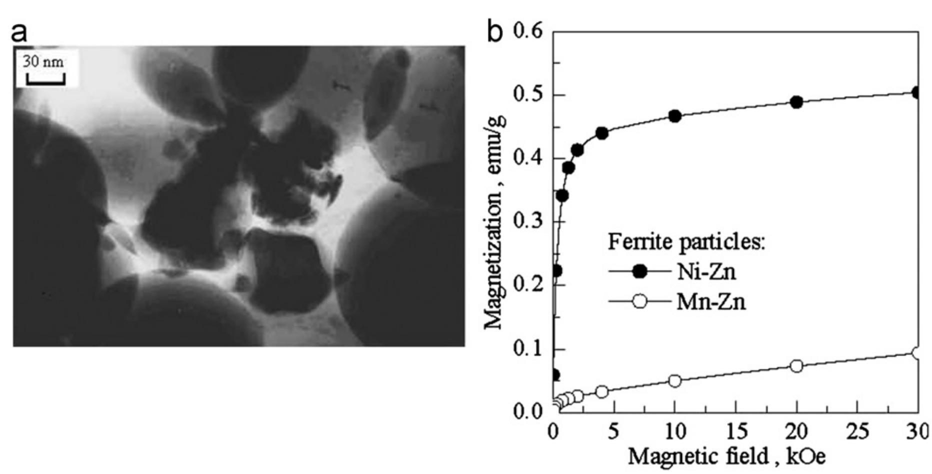

Fig. 1. (a) The dark-field TEM image of the 3D-nanocomposite with Ni–Zn ferrite-spinel particles and (b) the magnetization curve for the 3D-nanocomposite with Ni–Zn ferrite-spinel particles measured at room temperature.

not reached even in fields up to 30 kOe. The latter fact confirms the presence of superparamagnetic or strongly interacting particles. Thus the magnetic and structural data support the presence of additional phases. It is known that superparamagnetic properties are observed often in ferrite nanoparticles [16]. Magnetic properties of nanocrystalline NiCuZn ferrite particles were studied in the work of Su et al. [17].

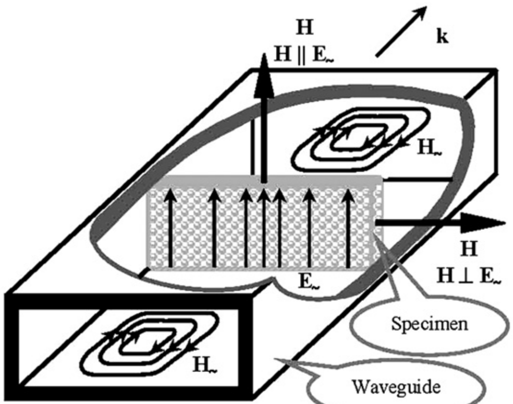

Fig. 2. Scheme of microwave measurements.

3. Microwave results

Microwave measurements have been carried out in the millimeter waveband in the frequency range from 26 to 38 GHz. The sample was placed inside a cross-section of the rectangular waveguide operating at the H_{10} mode(see Fig. 2). External permanent magnetic field H was applied perpendicular to the wave vector q. The field H lies typically in the plane of the sample perpendicularly to the vector of microwave magnetic field $H_{\sim}$. All microwave measurements were carried out at room temperature. Relative variation of the transmission coefficient in magnetic field was measured and was calculated according to the formula $d_m = [|D(H)| - |D(0)|] \ /|D(0)|$, where $|D(H)|$ is the transmission coefficient in magnetic field H. The relative variation of the reflection coefficient module was defined as $r_m = [|R(H)| - |R(0)|]/|R(0)|$, where $|R(H)|$ is the reflection coefficient.

External permanent magnetic field can essentially change the reflection and transmission coefficients of 3D-nanocomposites under investigation. It is usually assumed that the main reason for these variations is the magnetic resonance in ferrite particles. In this work we reveal another reason for strong microwave variations of the reflection and transmission coefficients apart from magnetic resonance. Let us discuss the magnetic field dependence of the reflection coefficient measured at different frequencies (Fig. 3a). At low frequencies in our band the shape of magnetic field dependence appears to be standard. The reflection coefficient lowers at first, reaches minimum and then increases.

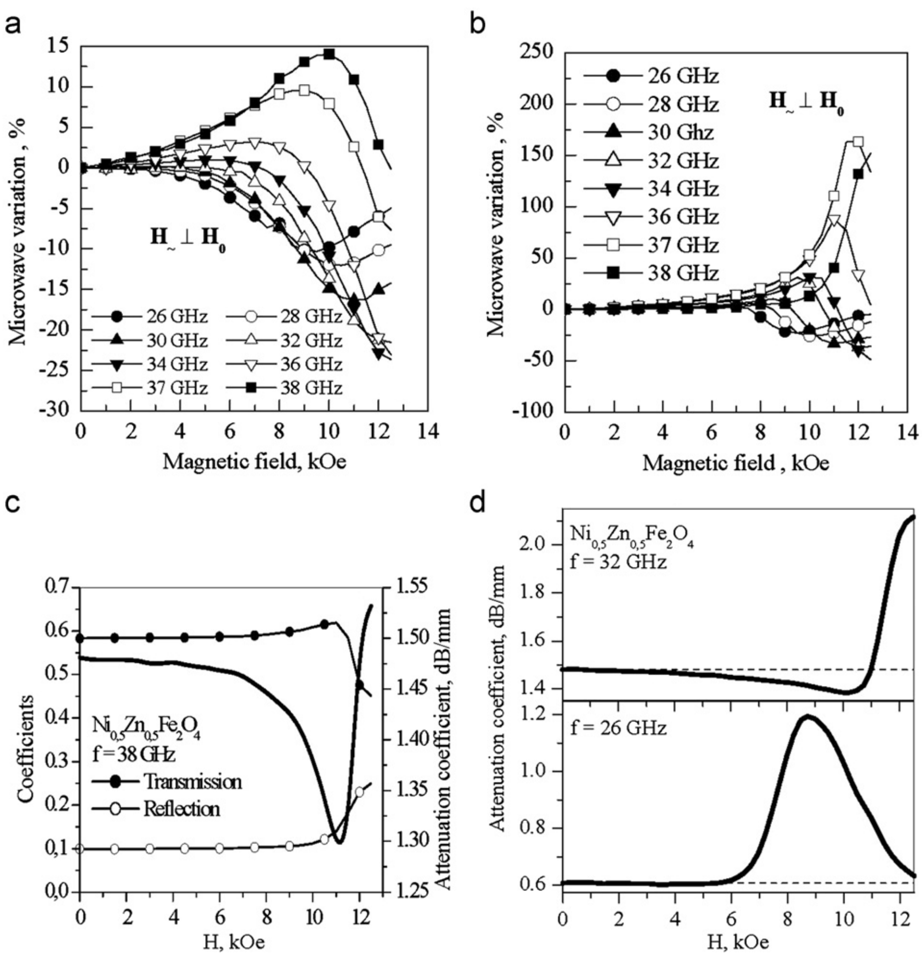

Fig. 3. Magnetic field dependence of the reflection coefficient module for the 3D-nanocomposites with the particles of $Co_{0.5}Zn_{0.5}Fe_2O_4$ (a) and $Ni_{0.5}Zn_{0.5}Fe_2O_4$ (b). Magnetic field dependence of the absolute values of the reflection and transmission coefficients for the 3D-nanocomposites with the particles of $Ni_{0.5}Zn_{0.5}Fe_2O_4$ (c); magnetic field dependence of the attenuation coefficients for the 3D-nanocomposites with the particles of $Ni_{0.5}Zn_{0.5}Fe_2O_4$ (d).

This behavior is typical of magnetic resonance and minima of the reflection and transmission coefficients are due to the great imaginary part of magnetic permeability. Actually, the resonance line for the 3D-nanocomposite is very wide since the ferrite particles are irregular in shape and are randomly oriented. Consequently, magnetization in different particles varies strongly from one particle to another. If the frequency exceeds 28 GHz, the reflection coefficient in magnetic fields, which are lower than the resonance field, first increases and then decreases after a maximum. This maximum especially clear for the 3D-nanocomposite with $Ni_{0.5}Zn_{0.5}Fe_2O_4$ particles (see Fig. 3b). At frequency of 37 GHz the magnitude of maximum exceeds 150%.

4. Discussion

In order to clarify the physical nature of abnormal maxima of the reflection coefficient, it is necessary to know how the absorbed electromagnetic power varies. For this purpose one should critically consider the modules of reflection $|R(H)|$ and transmission $|D(H)|$ coefficients measured at the same frequency and magnetic field. Magnetic field dependences of these coefficients measured at 38 GHz are shown in Fig. 3c. The difference $1-[|R(H)|+|D(H)|]$ corresponds to the fraction of electromagnetic losses in a sample. Being transformed into dB and normalized to 1 mm sample thickness, this difference corresponds to the attenuation coefficient. Its magnetic field dependence for the sample with $Ni_{0.5}Zn_{0.5}Fe_2O_4$ particles is also shown in Fig. 3c. The magnetic field dependence of attenuation coefficient for the 3D-nanocomposites with the particles of $Ni_{0.5}Zn_{0.5}Fe_2O_4$ measured at two frequencies, namely 26 and 36 GHz, is shown in Fig. 3d. It is clearly seen that at lower frequency of 26 GHz there is no minimum in the magnetic field dependence of the attenuation coefficient. At this frequency only magnetic resonance is seen. For the higher frequency of 36 GHz, however, a quite clearly seen minimum is evident in magnetic field less than the resonance maximum.

From the results presented, we can summarize the experimental conditions required to obtain the minimum of attenuation. Most definitely this minimum is seen for the 3D-nanocomposites with the particles of $Ni_{0.5}Zn_{0.5}Fe_2O_4$. The value of magnetic field for which the minimum is realized is always lower than the field of magnetic resonance. It has been experimentally confirmed that the minimum is observed only if the frequency exceeds a definite value, which is different for each nanocomposite. All these peculiarities allow us to classify this resonance minimum as an antiresonance. As is known from literature, minima in absorbed electromagnetic power can be obtained in magnetically ordered media under special conditions [18]. The antiresonance found in our work for the non-conducting 3D-nanocomposite, has some features very similar to the phenomena of antiresonance observed upon penetration of electromagnetic wave through a thin metallic film [19]. Probably, in our case the

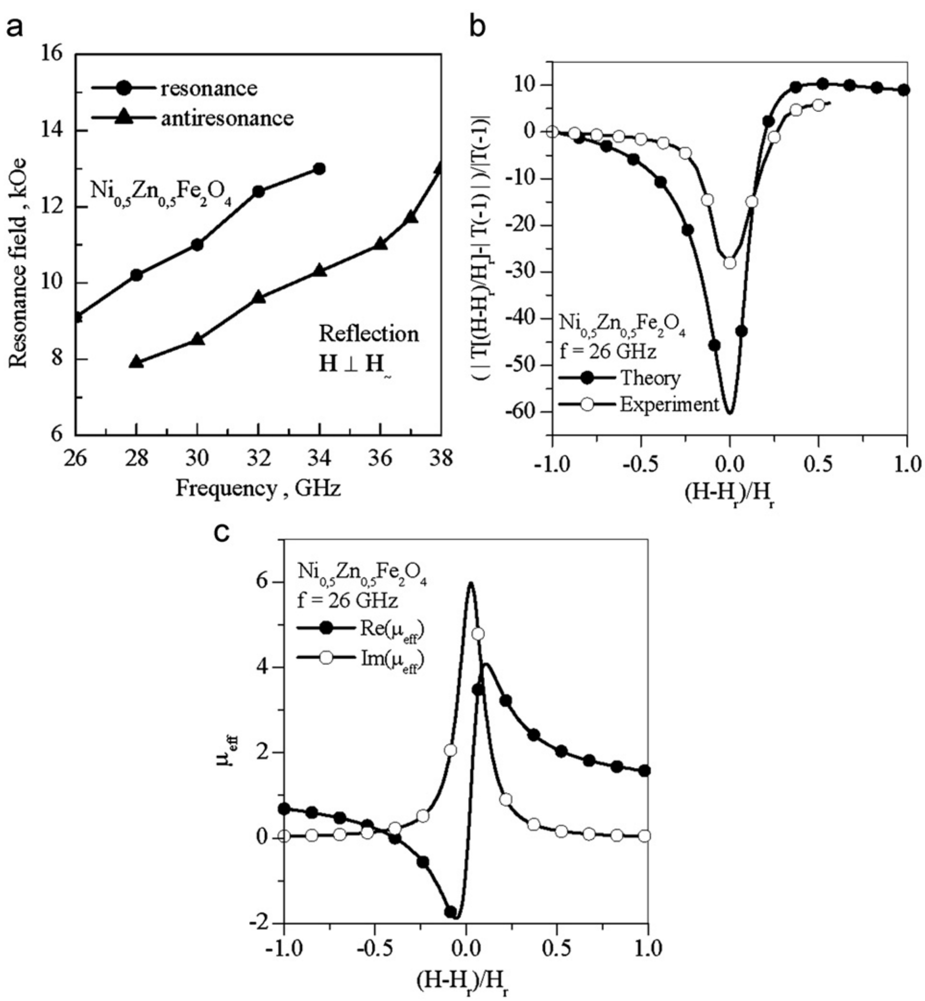

Fig. 4. (a) Spectra of magnetic resonance and antiresonance for the 3D-nanocomposites with the particles of $Ni_{0.5}Zn_{0.5}Fe_2O_4$; (b) the magnetic field dependence of the transmission coefficient at 26 GHz and (c) the magnetic field dependence of real and imaginary parts of magnetic permeability.

antiresonance occurs in magnetic field less than the resonance field in the vicinity of the point where the real part of magnetic permeability crosses zero. However, no exact similarity is observed since in the case of a metallic film close to the conditions of antiresonance the peculiarities of the imaginary part of magnetic permeability are small while the skin depth increases substantially. In our case we have minimum absorbed power and the antiresonance is caused by minimum dissipation. It is seen more clearly upon reflection rather upon transmission.

The spectra of resonance and antiresonance are shown in Fig. 4a. The branch of the spectrum corresponding to the antiresonance starts from the frequency of 28 GHz. The following question should be answered: whether the antiresonance can exist in a 3D-nanocomposite with non-conducting ferrite particles? Before answering positively, two items should be discussed. First, we can state that strong magnetic interaction exists between the ferrite particles inside the nanocomposite. We can confirm this statement from structural point of view since the distance between the individual particles in an aggregate can be very short. From magnetic data the presence of magnetically interacting particles can be confirmed by the shape of magnetization curve, in particular by the fact that the full saturation is not reached even in the high magnetic fields. Fulfillment of the second item, which consists in the necessity of zeroing the real part of magnetic permeability in a magnetic field smaller than the resonant one, is confirmed by the fact that magnetic permeability is negative in the fields close to and smaller the resonant one.

Magnetic field dependence of the effective magnetic permeability $\mu_{\text{eff}}=\mu_{\text{eff}}'-i\mu_{\text{eff}}''$ was extracted from the experimental dependence of the transmission coefficient measured at 26 GHz and is shown in Fig. 4b. As it is seen from Fig. 4c, the imaginary part has a sharp maximum at resonance and the real part of permeability is actually negative in the wide region, from $\sim 0.5H_{\text{r}}$ to H_{r} where H_{r} is the resonance field. At higher frequencies the resonance features in magnetic permeability will be definitely sharper. In the whole frequency range under investigation there will be a region near and less the resonance field where μ_{eff} is negative. Therefore all conditions necessary for antiresonance observation are fulfilled. While calculating the magnetic permeability one needs only the width of the resonance minimum in the transmission coefficient and the saturation magnetization value. The value of the resonance minimum can be taken from the microwave experimental data. In order to check the correctness of our calculations the magnetic field dependence of transmission coefficient was calculated using the permeability calculations under the known conditions such as magnetic field and frequency. These results were compared to the experimental ones and are presented in Fig. 4b. As it is seen from Fig. 4b, the complete agreement is absent but qualitative similarity of experimental and calculated curves can be clearly seen.

5. Conclusion

The electromagnetic properties of the opal matrix with the embedded ferrite-spinel nanoparticles have been studied in the millimeter waveband. Variations of the transmission and reflection coefficients are caused by two physical reasons—magnetic resonance and antiresonance. Magnetic antiresonance has been defined here as a minimum of absorbed power. The resonance-type variations of the reflection coefficient were modeled and it has been found that the magnetic resonance is related to the uniform branch of the magnetic resonance spectrum. The magnetic field dependence of the magnetic permeability tensor is determined, and it is proved that its diagonal component is negative in the interval of fields from the antiresonance to the resonance. The calculated and experimental dependences of the magnetic field variations of the transmission coefficient were compared and relatively close fit between them has been obtained which proves the correctness of the model proposed.

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